

# CHEMICAL EQUILIBRIUM

## 3.0 INTRODUCTION

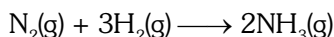
**Chemical reaction :** Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

**Types of chemical reaction :**

**(a) On the basis of physical state**

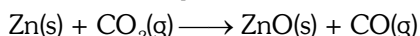
**(I) Homogeneous reactions**

All reactants and products are in same phase.



**(II) Heterogeneous reactions**

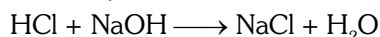
Reactants and products are in two or more phases.



**(b) On the basis of speed.**

**(I) Fast reactions**

(i) Generally these reactions are ionic reactions.

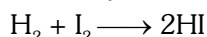


Acid    Base                  Salt    Water

(ii) Rate determination is almost impossible.

**(II) Slow reactions**

(i) Generally these reactions are molecular reactions.

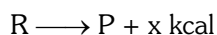


(ii) Rate determination is possible.

**(c) On the basis of heat**

**(I) Exothermic reactions**

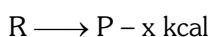
(i) Heat is evolved in these type of chemical reactions.



(ii) Change in enthalpy,  $\Delta H = (-)$  ve

**(II) Endothermic reactions**

Heat is absorbed in these type of chemical reactions.

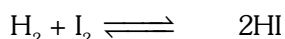
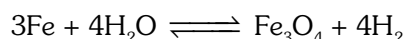
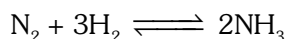


$\Delta H = (+)$  ve

**(d) On the basis of direction**

**(I) Reversible reactions**

(i) Chemical reaction in which products can be converted back into reactants.



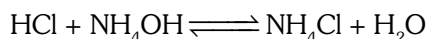
(ii) Proceed in forward as well as in backward direction.

(iii) Possible in closed container.

(iv) These can attain equilibrium.

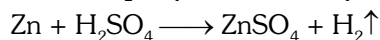
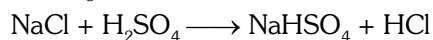
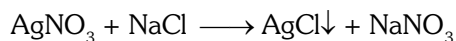
(v) Reactants are never completely converted into products.

(vi) Neutralisation reactions except of strong acid and strong base.

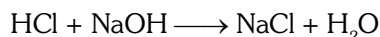


## (II) Irreversible reactions

- (i) Chemical reaction in which products cannot be converted back into reactants.



- (ii) Proceed only in one direction (forward direction).  
(iii) Generally possible in open container.  
(iv) These do not attain equilibrium.  
(v) Reactants are nearly completely converted into products.  
(vi) Neutralisation reactions of strong acid and strong base.



### GOLDEN KEY POINTS

- We always take forward direction if direction is not specified.
- In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice-versa.
- **Rate of Reaction**

The change in concentration of reactants or products in unit time is known as rate of the reaction.

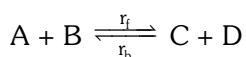
$$\text{Rate of reaction} = (\pm) \frac{\text{change in concentration}}{\text{time taken for the change}}$$

## 3.1 EQUILIBRIUM AND CHEMICAL PROCESS

### (A) Chemical Equilibrium

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium.

Consider a general reversible reaction in a closed vessel,



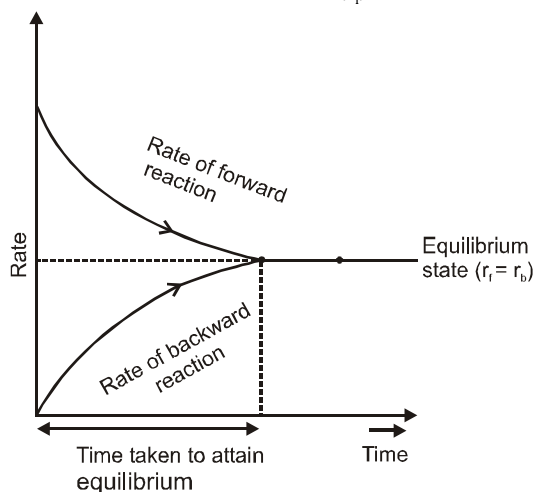
where,  $r_f$  = rate of forward reaction

$r_b$  = rate of backward reaction

Initially reaction occurs in forward direction but as the concentration of products increases reaction also starts in backward direction.

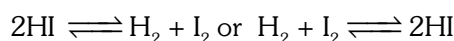
At a certain stage, rate of forward reaction becomes equal to the rate of backward reaction called equilibrium state.

**At equilibrium state :** Rate of forward reaction ( $r_f$ ) = Rate of backward reaction ( $r_b$ )



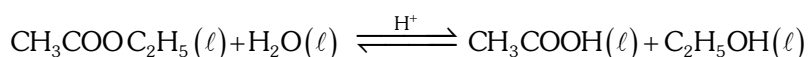
**(B) Characteristics of equilibrium :**

- The concentrations of the reactants and products do not change with time.
- At this stage, number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward reaction.
- Chemical equilibrium is dynamic in nature i.e. the reaction although appears to be stopped but actually takes place in both the directions with the same speed.
- Chemical equilibrium can be approached from both sides

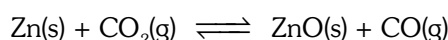


At equilibrium, each reactant and product has a constant concentration and this is independent of the fact whether the reaction starts from forward direction or backward direction with the reactant or with the product.

- Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- The measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the chemical equilibrium conditions.
- Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.



- Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.



- **ACTIVE MASS :** The term active mass means the concentration of the reactants expressed in moles per litre (molar concentration) or the pressure of the reacting gas in atmosphere. In case of gases and solutions, the molar concentration means the number of gram molecules present per litre.

Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [ ].

$$\begin{aligned}\text{Active mass} &= \frac{\text{Number of gram moles of the substance}}{\text{Volume(L)}} \\ &= \frac{\text{Weight of substance (in grams)}}{\text{Molecular weight (M}_w\text{)} \times \text{Volume (L)}} = \frac{w}{M_w \times V(\text{L})} = \frac{w \times 1000}{M_w \times V(\text{mL})}\end{aligned}$$

- The active mass of solids and pure liquids is a constant quantity (unity) because it is an intensive property i.e. number of molecules present per unit volume do not change because density and molecular weight of solids and pure liquids are constant. But it does not apply for gaseous substances because for them number of molecules present per unit volume change with change in volume of vessel.

$$\begin{aligned}\text{Molar concentration} &= \frac{w}{M_w \times V(\text{L})} = \frac{\rho}{M_w} \quad (\text{where } \rho = \text{density (in gL}^{-1}\text{)}) \\ &= \frac{\rho}{M_w} \times 1000 \quad (\text{where } \rho = \text{density (in gmL}^{-1}\text{)})\end{aligned}$$

$$\text{Active mass} = \frac{\text{density of the substance}}{\text{molecular mass of the substance}}$$



Following other names of active mass can also be used :

(i) mole/litre	(ii) gram mole/litre	(iii) gram molecules/litre
(iv) molarity	(v) Concentration	(vi) Effective concentration
(vii) active quantity	(viii) $n/v$	(ix) $C$
(x) $M$	(xi) $[ ]$	

## Illustrations

**Illustration 1.** In any chemical reaction, equilibrium is supposed to be established when :

- (1) Mutual opposite reaction undergo.
- (2) concentration of reactants and resulting products are equal.
- (3) Velocity of mutual reactions become equal.
- (4) The temperature of mutual opposite reactions becomes equal.

**Solution.** **Ans. (3)**

**Illustration 2.** **Assertion :** The active mass of pure solids and pure liquids is taken unity.

**Reason:** The active mass of pure solids and pure liquids depends on density and molecular mass. The density and molecular mass of pure solids and pure liquids are constant.

**Solution.** **Ans. (1)**

**Illustration 3.** 8.5 g ammonia is present in a vessel of 0.5 litre capacity then find out the active mass of ammonia?

**Solution.**  $[\text{NH}_3] = \frac{8.5}{17 \times 0.5} = 1 \text{ mol L}^{-1}$

### BEGINNER'S BOX-1

1. Which of the following statement is correct regarding with chemical equilibrium :-
  - (1) Based on extent to which the reactions proceed to reach the equilibrium we may have negligible concentrations of reactants are left
  - (2) Equilibrium is not static
  - (3) Concentration of reactants and products becomes constant at equilibrium
  - (4) All of these
2. Find out the correct statement :-
  - (1) Equilibrium condition is a state of reversible reaction
  - (2) Chemical equilibrium are important in numerous biological process like transport and delivery of  $\text{O}_2$
  - (3) Reversible reactions can be homogeneous and heterogeneous both
  - (4) All of these
3. Which of the following reaction is endothermic reaction :-
  - (1) Bond formation by two unstable atoms at certain condition
  - (2) Combustion reactions
  - (3) Conversion of more stable allotrope to less stable allotropic element
  - (4) Condensation of vapour to its liquid state
4. Active mass of 2 mol of NaCl kept in 4 litre vessel at NTP is :-
  - (1) 1
  - (2) 2
  - (3)  $\frac{1}{2}$
  - (4) Not defined

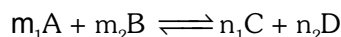


### 3.2 LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM

- The law of mass action was given by Guldberg and Waage (1864).
- It states that the rate of a chemical reaction is directly proportional to the product of active masses of the reacting substances raised to a power equal to the stoichiometric coefficient in the balanced chemical equation.

#### (A) Derivation of equilibrium constant :-

Consider a reversible homogeneous chemical reaction which has attained equilibrium state at a particular temperature :



Let the active masses of A, B, C and D be [A] [B] [C] and [D] respectively at equilibrium.

#### According to law of mass action :-

Rate of forward reaction  $(r_f) \propto [A]^{m_1} [B]^{m_2}$

Rate of backward reaction  $(r_b) \propto [C]^{n_1} [D]^{n_2}$

$$r_f = k_f[A]^{m_1}[B]^{m_2} \quad \text{and} \quad r_b = k_b[C]^{n_1}[D]^{n_2}$$

Where  $k_f$  and  $k_b$  are forward and backward rate or velocity constants respectively.

At equilibrium state –

$$r_f = r_b$$

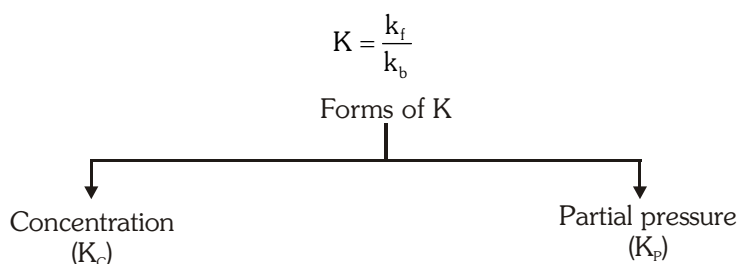
$$k_f[A]^{m_1}[B]^{m_2} = k_b[C]^{n_1}[D]^{n_2}$$

$$\frac{k_f}{k_b} = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

$$K = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \quad \therefore K = \frac{k_f}{k_b}$$

K is known as equilibrium constant and has a definite value for every chemical reaction at particular temperature.

- The equilibrium constant at a given temperature is the ratio of the rate constants of forward and backward reactions,



For reaction  $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_c = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

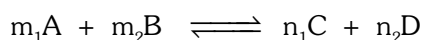
Unit of [ ] = mol L<sup>-1</sup>

$$K_p = \frac{(P_C)^{n_1} \times (P_D)^{n_2}}{(P_A)^{m_1} \times (P_B)^{m_2}}$$

Unit of P = atm.

#### (B) Relation between $K_p$ and $K_c$ :

Consider a reversible homogeneous chemical equilibrium reaction



According to law of mass action (LOMA)



$$K_C = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1} (P_D)^{n_2}}{(P_A)^{m_1} (P_B)^{m_2}}$$

For an ideal gas **PV = nRT**

Where – P = Pressure in atm  
V = Volume in litres  
n = Number of gaseous moles  
R = Gas constant = 0.0821 L atm mol<sup>-1</sup>k<sup>-1</sup>  
T = Temperature in kelvin

$$P = \frac{n}{V} RT = \text{active mass} \times RT$$

$$\frac{n}{V} = \text{molar concentration or active mass}$$

$$P_A = [A]RT, P_B = [B]RT, P_C = [C]RT \text{ and } P_D = [D]RT$$

Put all these values in  $K_P$  expression

$$\text{So } K_P = \frac{[C]^{n_1} (RT)^{n_1} \times [D]^{n_2} (RT)^{n_2}}{[A]^{m_1} (RT)^{m_1} \times [B]^{m_2} (RT)^{m_2}} = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}} \times \frac{(RT)^{n_1+n_2}}{(RT)^{m_1+m_2}}$$

$$K_P = K_C (RT)^{(n_1+n_2)-(m_1+m_2)}$$

$$\Delta n_g = (n_1 + n_2) - (m_1 + m_2)$$

= Sum of stoichiometric coefficient of gaseous products

– sum of stoichiometric coefficient of gaseous reactants

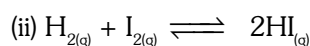
$$K_P = K_C (RT)^{\Delta n_g}$$

- The  $K_C$  is expressed by the units (mol L<sup>-1</sup>)<sup>Δn<sub>g</sub></sup> and  $K_P$  by (atm)<sup>Δn<sub>g</sub></sup>.
- Three cases may arise :-

**(a) When Δn<sub>g</sub> = 0**

$$K_P = K_C (RT)^0 = K_C$$

**For example :** (i)  $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

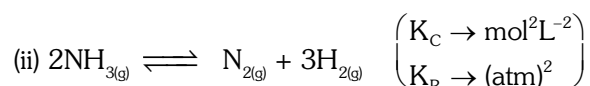


- $K_C$  and  $K_P$  are unit less in this case.

**(b) When Δn<sub>g</sub> = +ve**

$$K_P > K_C$$

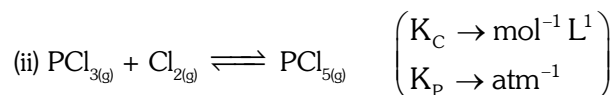
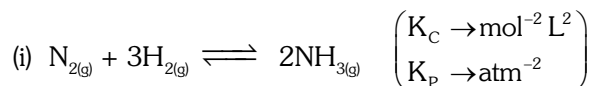
**For example :** (i)  $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \left( \begin{array}{l} K_C \rightarrow \text{mol L}^{-1} \\ K_P \rightarrow \text{atm} \end{array} \right)$



(c) When  $\Delta n_g = -ve$

$$K_p < K_c$$

For example :-



(d) Special point :

$$\text{If } T = \frac{1}{R} \text{ then}$$

$$K_p = K_c \left( R \times \frac{1}{R} \right)^{\Delta n_g}$$

$$K_p = K_c (1)^{\Delta n_g}$$

$$K_p = K_c$$

For any value of  $\Delta n_g$

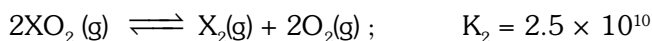
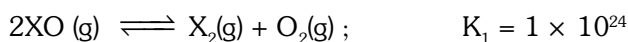
(C) Application of K -

Stability of reactants and products :

Stability of reactants increases when value of K decreases

Stability of products increases when value of K increases

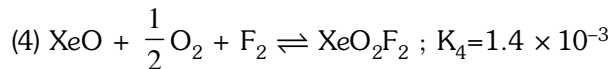
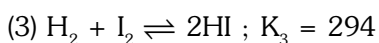
Ex : In the following reactions which one oxide is more stable.



$\therefore K_1 > K_2$  So the stability of  $XO_2 > XO$

## BEGINNER'S BOX-2

1. In which of the following reaction product is more stable :-



2. Equilibrium constant is :-

$$(1) \frac{k_b}{k_f}$$

$$(2) \frac{k_f}{k_b}$$

$$(3) k_f \times k_b$$

$$(4) \frac{1}{k_f k_b}$$

3. At 527°C, the reaction  $NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$  has  $K_c = 4$  then what is the value of  $K_p$  for the same reaction :-

$$(1) 16 \times (800 R)^2$$

$$(2) \left( \frac{800R}{4} \right)^{-2}$$

$$(3) \left( \frac{1}{4 \times 800 R} \right)^2$$

(4) None of these



4. For the equilibrium  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ , what is the temperature at which  $\frac{K_p(\text{atm})}{K_c(\text{M})} = 3$  :-

(1) 0.027 K

(2) 0.36 K

(3) 36.54 K

(4) 273 K

#### (D) Factors affecting the equilibrium constant –

(a) **Temperature** : The value of equilibrium constant changes with the change of temperature. If  $K_1$  and  $K_2$  be the equilibrium constants of a reaction at absolute temperatures  $T_1$  and  $T_2$  and  $\Delta H$  is the change in enthalpy then

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^0}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \text{ or } \log K_2 - \log K_1 = \frac{\Delta H^0}{2.303R} \left[ \frac{T_2 - T_1}{T_1 \cdot T_2} \right] \text{ (According to van't Hoff equation)}$$

If the temperature  $T_2$  is higher than  $T_1$  then  $\left( \frac{T_2 - T_1}{T_1 \cdot T_2} \right) > 0$ .

(i) When  $\Delta H = +ve$  (endothermic reaction)

$$\log K_2 - \log K_1 > 0 \Rightarrow \log K_2 > \log K_1$$

$$\Rightarrow K_2 > K_1$$

$\therefore$  The value of equilibrium constant increases when temperature increases in case of endothermic reactions.

(ii) When  $\Delta H = -ve$  (exothermic reaction)

$$\log K_2 - \log K_1 < 0$$

$$\Rightarrow \log K_2 < \log K_1$$

$$\Rightarrow K_2 < K_1$$

$\therefore$  The value of equilibrium constant decreases when temperature increases in the case of exothermic reactions.

#### (b) The mode of representation of the reaction :

Consider the reversible chemical equilibrium reaction  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$

$$\text{Equilibrium constant } K_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

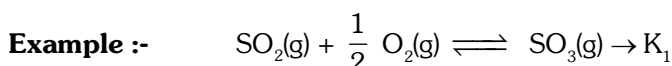
If the reaction is reversed  $\text{C} + \text{D} \rightleftharpoons \text{A} + \text{B}$

$$\text{Equilibrium constant } K'_c = \frac{[\text{A}][\text{B}]}{[\text{C}][\text{D}]}$$

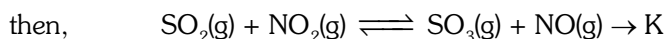
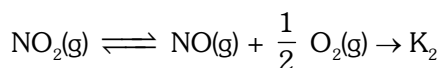
The equilibrium constant  $K'_c$  is actually the reciprocal of  $K_c$

$$\text{Thus, the two equilibrium constants are related as } \rightarrow K'_c = \frac{1}{K_c}$$

(c) **Multi step reaction** : If a reaction can be expressed as the sum of two or more reactions then overall  $K_c$  will be equal to the product of the individual equilibrium constants of the reactions.







So,  $K = K_1 \times K_2$

**(d) Stoichiometry of the reaction :-**

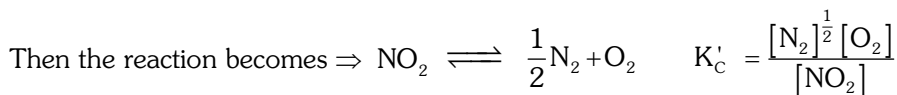
When a reversible reaction is multiplied or divided by a coefficient then the value of equilibrium constant will be numerically different in these cases.

For example the dissociation of  $\text{NO}_2$  can be represented as :



$$K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2}$$

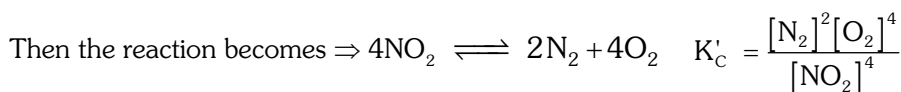
**(1) If reaction (i) is divided by 2 -**



Thus, the two equilibrium constants are related as  $K'_c = \sqrt{K_c}$

**So if reaction is divided by n then**  $K'_c = (K_c)^{\frac{1}{n}}$

**(2) If reaction (i) is multiplied by 2**



Thus, the two equilibrium constants are related as  $K'_c = (K_c)^2$

**So if reaction is multiplied by n then**  $K'_c = (K_c)^n$

## GOLDEN KEY POINTS

● **Factors not affecting the equilibrium constant :**

The value of equilibrium constant is independent of the following factors–

- |  |                                 |
|--|---------------------------------|
| (a) Concentration of reactants and products. | (b) Pressure                    |
| (c) Volume                                   | (d) The presence of a catalyst. |
| (e) Presence of inert materials.             |                                 |

● **The value of equilibrium constant depends only on temperature.**

## Illustrations

**Illustration 4.**  $\text{XeF}_6 + \text{H}_2\text{O} \rightleftharpoons \text{XeOF}_4 + 2\text{HF}$  constant =  $K_1$ ,  $\text{XeO}_4 + \text{XeF}_6 \rightleftharpoons \text{XeOF}_4 + \text{XeO}_3\text{F}_2$  constant =  $K_2$ . Then equilibrium constant for the reaction  $\text{XeO}_4 + 2\text{HF} \rightleftharpoons \text{XeO}_3\text{F}_2 + \text{H}_2\text{O}$  will be–

- |                       |                 |                       |                           |
|-----------------------|-----------------|-----------------------|---------------------------|
| (1) $\frac{K_1}{K_2}$ | (2) $K_1 + K_2$ | (3) $\frac{K_2}{K_1}$ | (4) $\frac{K_1}{(K_2)^2}$ |
|-----------------------|-----------------|-----------------------|---------------------------|

**Solution**

**Ans. (3)**



- Illustration 5** **Assertion:-** In the presence of catalyst, the value of equilibrium constant K increases.  
**Reason :-** Catalysts increases the rate of forward and backward reaction to same extent.  
 (1) A (2) B (3) C (4) D
- Solution** **Ans. (4)**

### 3.3 DEGREE OF DISSOCIATION

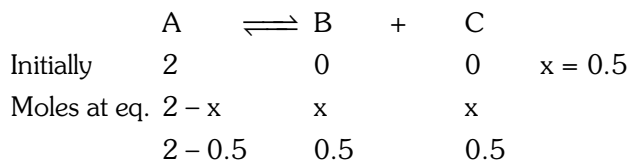
It is the fraction of moles of reactant dissociated  $\alpha = \frac{x}{a}$   
 $\% \alpha = \frac{x}{a} \times 100$

Where  $\alpha$  = Degree of dissociation  
 $x$  = Number of dissociated moles  
 $a$  = Initial number of moles (given)

### Illustrations

- Illustration 6** 40% of  $\text{PCl}_5$  is not dissociated at  $300^\circ\text{C}$ . The reaction is carried out in a flask of 1 litre capacity. The value of  $K_c$  would be :-  
 (1) 3.2 (2) 1.6 (3)  $(3.2)^{-1}$  (4) 0.9
- Solution** **Ans. (4)**

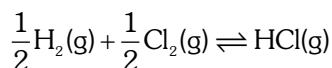
- Illustration 7** In the beginning of the reaction,  $\text{A} \rightleftharpoons \text{B} + \text{C}$ , 2 moles of A are taken, out of which 0.5 moles gets dissociated. What is the amount of dissociation of A ?  
 (1) 0.5 (2) 1 (3) 0.25 (4) 4.2
- Solution** **Ans. (3)**



Since, two moles dissociated into 0.5  
 Therefore, one mole will dissociated into 0.25

### BEGINNER'S BOX-3

1. The equilibrium constant ( $K_c$ ) for the reaction  $2\text{HCl(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$  is  $4 \times 10^{-34}$  at  $25^\circ\text{C}$ . What is the equilibrium constant for the reaction :-



- (1)  $2 \times 10^{-17}$  (2)  $2.5 \times 10^{33}$  (3)  $5 \times 10^6$  (4) None of these
2. Consider the following gaseous equilibrium given below  
 I.  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  ; eq. constant =  $K_1$  II.  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$  ; eq. constant =  $K_2$   
 III.  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  eq. constant =  $K_3$

The equilibrium constant for the reaction  $2\text{NH}_3 + \frac{5}{2}\text{O}_2 \rightleftharpoons 2\text{NO} + 3\text{H}_2\text{O}$  in terms of  $K_1$ ,  $K_2$  and  $K_3$  will be :-

- (1)  $K_1 K_2 K_3$  (2)  $\frac{K_1 K_2}{K_3}$  (3)  $\frac{K_1 K_3^2}{K_2}$  (4)  $\frac{K_2 K_3^3}{K_1}$



3. Using molar concentrations, what is the unit of  $K_c$  for the reaction  $\text{CH}_3\text{OH(g)} \rightleftharpoons \text{CO(g)} + 2\text{H}_2\text{(g)}$  :-  
 (1)  $\text{M}^{-2}$  (2)  $\text{M}^2$  (3)  $\text{M}^{-1}$  (4)  $\text{M}$
4. If temperature is increased then equilibrium constant will be :-  
 (1) Increased  
 (2) Decreased  
 (3) Remains constant  
 (4) May increased or decreased depends on exothermic or endothermic nature
5. What will be the equilibrium constant at  $127^\circ\text{C}$ . If equilibrium constant at  $27^\circ\text{C}$  is 4 for reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ;  $\Delta H = -46.06 \text{ kJ}$  :-  
 (1)  $4 \times 10^{-2}$  (2)  $2 \times 10^{-3}$  (3)  $10^2$  (4)  $4 \times 10^2$
6. In which of the following equilibrium equation,  $K_p > K_c$   
 (1)  $2\text{SO}_3\text{(g)} \rightleftharpoons 2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$  (2)  $\text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{PCl}_5\text{(g)}$   
 (3)  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$  (4)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$
7. If  $\text{CoO(s)} + \text{H}_2\text{(g)} \rightleftharpoons \text{Co(s)} + \text{H}_2\text{O(g)}$ ,  $K_1 = 60$ ;  $\text{CoO(s)} + \text{CO(g)} \rightleftharpoons \text{Co(s)} + \text{CO}_2\text{(g)}$ ,  $K_2 = 180$  then the equilibrium constant of the reaction  $\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)}$  will be—  
 (1) 0.44 (2) 0.11 (3) 0.22 (4) 0.33

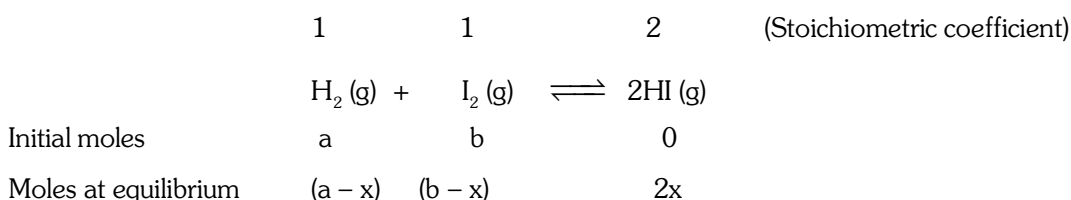
### 3.4 APPLICATIONS OF LAW OF MASS ACTION

#### [Relation of dissociation (x) with volume (V) and pressure (P)]

##### (A) Homogeneous Gaseous Reactions of Type-I ( $\Delta n_g = 0$ )

##### Synthesis of HI :-

- (i) **Expression for  $K_c$**  : The formation of HI from  $\text{H}_2$  and  $\text{I}_2$  is represented by following reaction



Let us start with 'a' moles of  $\text{H}_2$  and 'b' moles of  $\text{I}_2$  in a closed bulb of V volume. If at equilibrium x moles of each of  $\text{H}_2$  and  $\text{I}_2$  have reacted, then 2x moles of HI will be formed so active masses.

$$[\text{H}_2] = \frac{(a-x)}{V}; [\text{I}_2] = \frac{(b-x)}{V}; [\text{HI}] = \frac{2x}{V}$$

Applying law of mass action

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$\Rightarrow K_c = \frac{4x^2}{(a-x)(b-x)}$$



- When  $a = b = 1$ ,  $x$  becomes degree of formation of HI or degree of dissociation of  $H_2$ (or  $I_2$ ).  $K_C = \frac{4x^2}{(1-x)^2}$

Let if  $x \ll 1$  then  $1-x \approx 1$  So  $K_C = 4x^2$

$$x = \sqrt{\frac{K_C}{4}} \quad \text{i.e.} \quad \boxed{x \propto V^0}$$

At equilibrium the degree of dissociation is independent to the volume.

- (ii) **Expression for  $K_p$**  : The equilibrium constant  $K_p$  can also be calculated considering partial pressures of reactants and products at equilibrium.

Total number of moles at equilibrium =  $(a-x) + (b-x) + 2x = (a+b)$

If total pressure of the system at equilibrium be  $P$  then

Partial pressure of  $H_2 = \frac{(a-x)}{(a+b)} P$  ; Partial pressure of  $I_2 = \frac{(b-x)}{(a+b)} P$  ; Partial pressure of HI =  $\frac{2x}{(a+b)} P$

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{\left(\frac{2x}{a+b} P\right)^2}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right) P^2}$$

$$K_p = \frac{4x^2}{(a-x)(b-x)} \quad \text{Thus } K_p = K_C$$

Let if  $x \ll 1$  then  $1-x \approx 1$  So  $K_p = 4x^2$

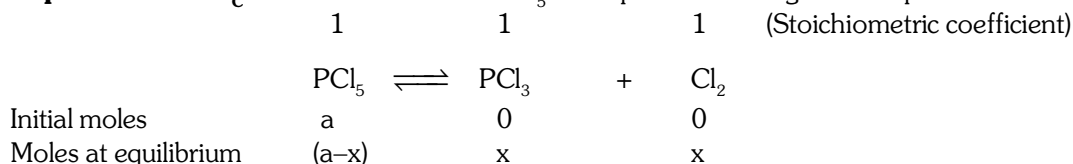
$$x = \sqrt{\frac{K_p}{4}} \quad \text{i.e.} \quad \boxed{x \propto P^0}$$

At equilibrium the degree of dissociation is independent to the pressure also.

## (B) Homogeneous Gaseous reactions of Type-II ( $\Delta n_g > 0$ )

### Dissociation of $PCl_5$ :-

- (i) **Expression for  $K_C$**  : The dissociation of  $PCl_5$  takes place according to the equation



Let  $a$  moles of  $PCl_5$  be taken in a closed vessel of volume  $V$ . At equilibrium  $x$  moles of  $PCl_5$  are dissociated into  $x$  moles of each  $PCl_3$  and  $Cl_2$ .

$$[PCl_5] = \frac{(a-x)}{V} \quad ; \quad [PCl_3] = \frac{x}{V} \quad ; \quad [Cl_2] = \frac{x}{V}$$

$$\text{Apply law of mass action } K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

- When  $a = 1$ ,  $x$  becomes degree of dissociation( $\alpha$ )  $K_C = \frac{\alpha^2}{(1-\alpha)V}$

$$\text{If } \alpha \ll 1 \text{ then } 1-\alpha \approx 1 \quad K_C \approx \frac{\alpha^2}{V} \quad \text{or} \quad \boxed{\alpha \propto \sqrt{V}}$$

The degree of dissociation of  $PCl_5$  at equilibrium is directly proportional to the square root of the volume.



**(ii) Expression for  $K_p$  :**

Let the total pressure at equilibrium be  $P$ .

Total number of moles at equilibrium =  $(a - x) + x + x = a + x$

$$p_{\text{PCl}_5} = \left(\frac{a-x}{a+x}\right)P, \quad p_{\text{PCl}_3} = \left(\frac{x}{a+x}\right)P, \quad p_{\text{Cl}_2} = \left(\frac{x}{a+x}\right)P$$

Apply law of mass action 
$$K_p = \frac{p_{\text{PCl}_3} \cdot p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{x^2 P}{(a+x)(a-x)}$$

When  $a = 1$ ,  $x$  becomes degree of dissociation ( $\alpha$ ) 
$$K_p = \frac{\alpha^2 P}{(1+\alpha)(1-\alpha)} = \frac{\alpha^2 P}{1-\alpha^2}$$

If  $\alpha \ll 1$  then  $1 - \alpha^2 \approx 1$ ,  $K_p \approx \alpha^2 P$

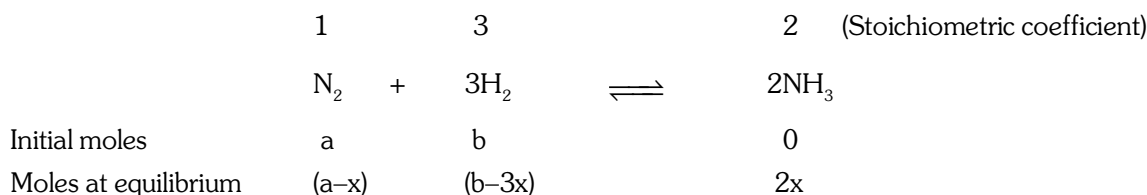
$$\alpha^2 \propto \frac{1}{P} \Rightarrow \boxed{\alpha \propto \frac{1}{\sqrt{P}}}$$

- The degree of dissociation of  $\text{PCl}_5$  is inversely proportional to the square root of the total pressure at equilibrium.

**(C) Homogeneous Gaseous reactions of Type-III ( $\Delta n_g < 0$ )**

**Synthesis of Ammonia :-**

- (i) Expression for  $K_c$  :** The formation of ammonia from nitrogen and hydrogen is represented by the equation :



Let us start with 'a' moles of  $\text{N}_2$  and 'b' moles of  $\text{H}_2$  in a closed vessel of Volume  $V$ . At equilibrium  $x$  moles of  $\text{N}_2$  has combined with  $3x$  moles of  $\text{H}_2$  and produced  $2x$  moles of  $\text{NH}_3$ .

At equilibrium 
$$[\text{N}_2] = \frac{(a-x)}{V}; \quad [\text{H}_2] = \frac{(b-3x)}{V}; \quad [\text{NH}_3] = \frac{2x}{V}$$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

If  $a = 1$ ,  $b = 3$  then 
$$K_c = \frac{4x^2 V^2}{27(1-x)^4}$$

If  $x \ll 1$  then  $1 - x \approx 1$

$$K_c = \frac{4x^2 V^2}{27} \quad \text{i.e.} \quad \boxed{x \propto \frac{1}{V}}$$

At equilibrium, the degree of dissociation is inversely proportional to the volume of vessel.



**(ii) Expression for  $K_p$  :-**

Total number of moles at equilibrium =  $a - x + b - 3x + 2x = a + b - 2x$

If total pressure is  $P$  at equilibrium then

$$p_{N_2} = \frac{(a-x)}{(a+b-2x)}P, \quad p_{H_2} = \frac{(b-3x)}{(a+b-2x)}P, \quad p_{NH_3} = \frac{2x}{(a+b-2x)}P$$

According to Law of mass action

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{\left(\frac{2x}{a+b-2x}P\right)^2}{\left(\frac{a-x}{a+b-2x}\right)\left(\frac{b-3x}{a+b-2x}\right)^3}$$

$$K_p = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

$$\text{If } a = 1, b = 3 \text{ then } K_p = \frac{16x^2(2-x)^2}{27(1-x)^4 P^2}$$

If  $x \ll 1$  then  $2-x \approx 2$  and  $1-x \approx 1$

$$K_p = \frac{64x^2}{27P^2} \text{ i.e. } x^2 \propto P^2 \Rightarrow \boxed{x \propto P}$$

At equilibrium, the degree of dissociation is directly proportional to the pressure.

**GOLDEN KEY POINTS**

- If inert gas mixed at constant temperature and constant volume in an equilibrium chemical reaction then total number of moles of gases are present in a container increases i.e. total pressure of gases increases but concentration in terms of  $\text{mol L}^{-1}$  and partial pressure of reacting substances are unchanged so dissociation ( $x$ ) unchanged.

- $\alpha \propto (V)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$  or  $\alpha \propto \left(\frac{1}{P}\right)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$

Effect	$\Delta n_g = 0$ $H_2 + I_2 \rightleftharpoons 2HI$ $x \propto (v)^\circ \propto (P)^\circ$	$\Delta n_g > 0$ or +ve $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $x \propto (v)^{1/2} \propto \left(\frac{1}{P}\right)^{1/2}$	$\Delta n_g < 0$ or -ve $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $x \propto \left(\frac{1}{v}\right) \propto (P)$
(i) Pressure (increases)	$x$ unchanged	$x$ decreases	$x$ increases
(ii) Volume (increases)	$x$ unchanged	$x$ increases	$x$ decreases
(iii) Mixing of inert gas at			
(a) constant pressure	$x$ unchanged	$x$ increases	$x$ decreases
(b) constant volume	$x$ unchanged	$x$ unchanged	$x$ unchanged



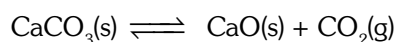
**BEGINNER'S BOX-4**

1.  $A + B \rightleftharpoons C + D$  If initially of A and B are both are taken in equal amount but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction :-  
 (1)  $\frac{4}{9}$  (2)  $\frac{9}{4}$  (3)  $\frac{1}{9}$  (4) 4
2. At a certain temperature, only 50% HI is dissociated at equilibrium in the reaction  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$  The equilibrium constant for the reaction is :-  
 (1) 0.25 (2) 1.0 (3) 3.0 (4) 0.5
3. The equilibrium constant  $K_p$  for the reaction  $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$  is 4.0 at 1660°C. Initially 0.80 mole  $H_2$  and 0.80 mole  $CO_2$  are injected into a 5.0 liter flask. What is the equilibrium concentration of  $CO_2(g)$  :-  
 (1) 0.533 M (2) 0.0534 M  
 (3) 5.34 M (4) None of these
4.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  for the reaction initially the mole ratio was 1 : 3 of  $N_2$  :  $H_2$ . At equilibrium 50% of each has reacted. If the equilibrium pressure is p, the partial pressure of  $NH_3$  at equilibrium is :-  
 (1)  $\frac{p}{3}$  (2)  $\frac{p}{4}$  (3)  $\frac{p}{6}$  (4)  $\frac{p}{8}$
5. For the reaction  $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ , if the initial concentration of  $[H_2] = [CO_2]$  and x moles/litre of hydrogen is consumed at equilibrium, the correct expression of  $K_p$  is :-  
 (1)  $\frac{x^2}{(1-x)^2}$  (2)  $\frac{(1+x)^2}{(1-x)^2}$  (3)  $\frac{x^2}{(2+x)^2}$  (4)  $\frac{x^2}{1-x^2}$

**(D) Law of Mass Action as Applied to Heterogeneous Equilibrium :-**

In such cases the active mass of pure solids and pure liquids is taken as unity and the value of equilibrium constant is determined by the gaseous substances only.

- (i) The dissociation of  $CaCO_3$  in closed vessel.



$$K_p = p_{CO_2}$$

- (ii)  $2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

$$K_p = (p_{H_2})^2 (p_{O_2})$$

- (iii)  $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$$K_p = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$$



## Illustrations

**Illustration 8** Two sample of HI each of 5 g were taken separately into vessels of volume 5 and 10 litres respectively at 27°C. The extent of dissociation of HI will be :-

- (1) More in 5 litre vessel (2) More in 10 litre vessel  
(3) Equal in both vessel (4) None of these

**Solution** **Ans. (3)**

**Illustration 9** What will be the amount of dissociation, if the volume is increased 16 times of initial volume in the reaction  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$  ?

- (1) 4 times (2)  $\frac{1}{4}$  times  
(3) 2 times (4)  $\frac{1}{5}$  times

**Solution** **Ans. (1)**

$x \propto \sqrt{V}$  or  $x \propto \sqrt{16}$  Thus, 4 times.

**Illustration 10** **Assertion:-** For the reaction,  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ , increase in pressure at equilibrium has no effect on the reaction.

**Reason :-** The reaction is not accompanied by any change in number of moles of gaseous species.

- (1) A (2) B (3) C (4) D

**Solution** **Ans. (1)**

### 3.5 LE-CHATELIER'S PRINCIPLE

**PRINCIPLE :-** According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

- Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

#### (A) CHEMICAL EQUILIBRIUM

##### (a) Change in concentration:-

In an equilibrium increasing the concentrations of reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of the reactants.

##### (b) Change in pressure :-

When the pressure on the system is increased, the volume decreases proportionately i.e. the total number of moles present per unit volume increases. According to Le-Chatelier's principle, the equilibrium shifts in that direction in which there is decrease in number of moles.

- If there is no change in number of moles of gases in a reaction then a pressure change does not affect the equilibrium.

##### (c) Change in temperature :-

If the temperature of the system at equilibrium is increased then reaction will proceed in that direction in which heat can be used. Thus increase in temperature will favour the forward reaction for endothermic reaction.

Similarly, increase in temperature will favour the backward reaction for exothermic reactions.





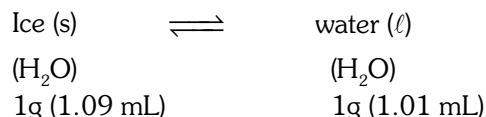
## (B) PHYSICAL EQUILIBRIUM

**Physical reaction :-** Those reaction in which change in only and only physical states (solid, liquid and gas) of substance takes place without any chemical change, is called physical reaction.

**Example :**

### (a) Ice-water system (melting of ice) :

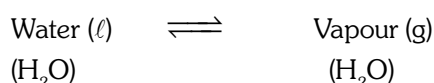
Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume



Hence both increase of temperature and pressure will favour the melting of ice into water.

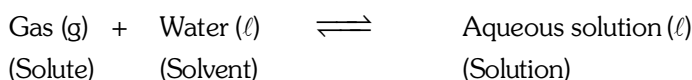
### (b) Water-water vapour system (Vapourisation of water) :

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic reaction:



- The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.
- The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.
- Thus favourable conditions for conversion of water into vapour are high temperature and low pressure.

### (c) Solubility of gases :



- **Effect of pressure** → Solubility of such gases increases with increasing pressure which dissolves in a solvent with a decrease in volume.

## Illustrations

**Illustration 11** On applying pressure to the equilibrium  $\text{ice} \rightleftharpoons \text{water}$ , which phenomenon will happen :

- (1) More ice will be formed
- (2) More water will be formed
- (3) Equilibrium will not be disturbed
- (4) Water will evaporate

**Solution** **Ans. (2)**

**Illustration 12** Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium  $\text{H}_2 \rightleftharpoons \text{H} + \text{H}$  ( $\Delta H = +ve$ ) ?

- (1) 2000° C temperature and 760 mm of Hg pressure.
- (2) 3500° C temperature and 100 cm of Hg pressure.
- (3) 3500° C temperature and 1 mm of Hg pressure.
- (4) All are wrong.

**Solution** **Ans. (3)**

In  $\text{H}_2 \rightleftharpoons \text{H} + \text{H}$ , heat has to be provided to dissociate  $\text{H}_2$  into  $\text{H}$ . Therefore, the reaction is endothermic ( $\Delta H$  will positive). So, temperature should be high. Since, one mole of  $\text{H}_2$  forms two atoms of  $\text{H}$ , so volume is increasing ( $\Delta n$  is positive) so pressure should be low for increasing the rate of forward reaction.



**Illustration 13 Assertion :**  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{heat}$  ; Forward reaction is favoured at low temperature and high pressure.

**Reason :** Reaction is endothermic.

- (1) A (2) B (3) C (4) D

**Solution Ans. (3)**

**Illustration 14.** The reaction  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  goes to completion in lime kiln because :

- (1) of the high temperature (2) CaO is more stable than  $\text{CaCO}_3$   
(3) CaO is not dissociated (4)  $\text{CO}_2$  escapes continuously

**Solution Ans. (4)**

**Illustration 15. Assertion:** For a reversible exothermic reaction, extent of reaction decreases with increase in temperature.

**Reason:** In reversible exothermic reaction temperature is favourable for more formation of product.

**Solution Ans. (3)**

### BEGINNER'S BOX-5

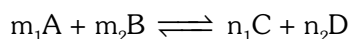
- Which of the following equilibrium remains unaffected by a change in pressure (or volume) ?  
 (1)  $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{s}) + \text{Cl}_2(\text{g})$  (2)  $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$   
 (3)  $3\text{PbS}(\text{s}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{PbO}(\text{s}) + 2\text{SO}_2(\text{g})$  (4)  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- Consider the following equilibrium system;  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ ; some inert gas is added to the above system at constant volume. Predict which of the following is true?  
 (1) More of  $\text{SO}_3$  is produced.  
 (2) Less  $\text{SO}_2$  is produced.  
 (3) Addition of inert gas does not affect equilibrium.  
 (4) system moves to new equilibrium position which cannot be predicted theoretically.
- Which of the following is not true for the equilibrium reaction;  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ ;  $\Delta H = 180 \text{ kJ mol}^{-1}$ .  
 (1) the formation of NO is increased at higher temperature.  
 (2) The volume change at constant pressure does not affect the equilibrium.  
 (3) The pressure change at constant volume does not affect the equilibrium.  
 (4) The formation of NO is decreased at higher temperature.
- Consider the following equilibrium system;  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$ ; set up in a cylinder fitted with a piston. Some inert gas is added and the piston is moved outwards to keep the total gaseous pressure constant. Predict which of the following is true?  
 (1) Addition of inert gas does not affect the equilibrium.  
 (2) Less  $\text{SO}_3(\text{g})$  is produced.  
 (3) More  $\text{SO}_3(\text{g})$  is produced.  
 (4) The system moves to new equilibrium position which cannot be predicted theoretically.
- When a volatile liquid is introduced into an evacuated closed vessel at a particular temperature, both evaporation and condensation take place simultaneously. The system reaches equilibrium state when—  
 (1) The liquid is completely transformed into the corresponding vapour  
 (2) Equal amounts of liquid and vapour are present in the system  
 (3) The rate of evaporation becomes equal to the rate of condensation  
 (4) Liquid cannot be converted into vapour and vice versa.
- Which of the following equilibrium is dynamic ?  
 (1)  $\text{Solid} \rightleftharpoons \text{Liquid}$  (2)  $\text{Liquid} \rightleftharpoons \text{Vapor}$  (3)  $\text{Solid} \rightleftharpoons \text{Vapor}$  (4) All of these



7. Which of the following is not true for solid-liquid equilibrium ?
- (1) It can be established at any given temperature.
  - (2) The mass of solid does not change with time.
  - (3) The mass of liquid does not change with time.
  - (4) There is no exchange of heat between the system and its surrounding.
8. Which of the following substances can be placed in a closed vessel to establish (solid  $\rightleftharpoons$  vapour) equilibrium?
- (1) Ammonium chloride    (2) Camphor    (3) Iodine    (4) All of these
9. Which of the following solutions kept in contact with undissolved solute is an example of solid-solution equilibrium?
- (1) Aqueous solution    (2) Saturated solution    (3) Unsaturated solution    (4) Nonaqueous solution
10. Which of the following is correct regarding the gas-solution equilibrium ?
- (1) The solubility of the dissolved gas increases with the increase of pressure and decreases with the increase of temperature.
  - (2) The solubility of the dissolved gas increases with the increase of pressure as well as temperature.
  - (3) The solubility of the dissolved gas decreases with the increase of pressure and increases with the increase of temperature.
  - (4) The solubility of the dissolved gas decreases with the increase of pressure as well as temperature.

### 3.6 REACTION QUOTIENT (Q)

Consider a general homogeneous reversible reaction :



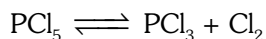
$$\text{Reaction Quotient (Q)} = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}, \quad (\text{Applied at any stage of reaction})$$

$$\text{Equilibrium constant K} = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}, \quad (\text{Applied only at equilibrium state})$$

- (i) When  $Q = K$  then reaction is in equilibrium state.
- (ii) When  $Q < K$  then rate of forward reaction increases.
- (iii) When  $Q > K$  then rate of backward reaction increases.

### 3.7 Calculation of degree of dissociation from vapour density :-

Ex.



$$\alpha = \frac{D_T - D_0}{D_0} = \frac{D - d}{d}$$

**Where :**  $D_T$  or  $D$  = Principle or theoretical vapour density or normal vapour density  
 $D_0$  or  $d$  = Observed or practical vapour density or experimental vapour density at higher temp.  
 $\alpha$  = Degree of dissociation

$\text{Vapour density} = \frac{\text{Molecular weight}}{2}$
---



Reversible reaction	$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$	Total moles	Volume at NTP	Vapour density
Let initial moles	1            0            0	1	$V_T = 22.4$	$D_T \propto \frac{1}{V_T}$
Moles at equilibrium	$(1-\alpha)$ $\alpha$ $\alpha$	$1+\alpha$	$V_0 = 22.4(1+\alpha)$	$D_0 \propto \frac{1}{V_0}$

If  $\alpha$  is the degree of dissociation

$$\frac{D_T}{D_0} = \frac{V_0}{V_T} = \frac{22.4(1+\alpha)}{22.4}$$

$$\frac{D_T}{D_0} = 1 + \alpha \quad \text{or} \quad \alpha = \frac{D_T}{D_0} - 1 \quad \boxed{\alpha = \frac{D_T - D_0}{D_0}}$$

So for a general reversible reaction  $n_1 A \rightleftharpoons n_2 B + n_3 C$

$$\alpha = \frac{n_1}{\Delta n} \left( \frac{D_T - D_0}{D_0} \right) \quad \Delta n = (n_2 + n_3) - (n_1)$$

OR

$$\alpha = \frac{n_1}{\Delta n} \left( \frac{M_T - M_0}{M_0} \right)$$

$M_T$  = Theoretical molecular weight

$M_0$  = Observed or experiment molecular weight

## Illustrations

**Illustration 16** The vapour density of undecomposed  $\text{N}_2\text{O}_4$  is 46. When heated, vapour density decreases to 24.5 due to its dissociation to  $\text{NO}_2$ . The percentage dissociation of  $\text{N}_2\text{O}_4$  at the final temperature is -  
 (1) 87                                      (2) 60                                      (3) 40                                      (4) 70

**Solution**                                      **Ans. (1)**

**Illustration 17** If  $\text{PCl}_5$  is 80% dissociated at  $250^\circ \text{C}$  then its vapour density at room temperature will be  
 (1) 56.5                                      (2) 104.25                                      (3) 101.2                                      (4) 52.7

**Solution**                                      **Ans. (2)**

$$\alpha = \frac{D_T - D_0}{D_0}; \quad D_T = \frac{\text{Molecular weight}}{2}$$

Vapour density at room temperature ( $D_T$ ) is 104.25, which is fixed.

**Illustration 18** **Assertion:-** For a reaction, reaction quotient (Q) is equal to K when the reaction is in equilibrium.

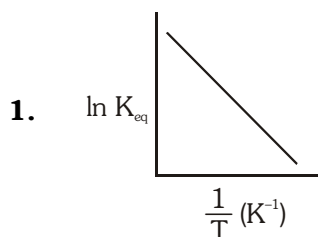
**Reason:-** If a catalyst is added to the reaction at equilibrium, the value of Q remains no longer equal to K.

(1) A                                      (2) B                                      (3) C                                      (4) D

**Solution**                                      **Ans. (3)**



## BEGINNER'S BOX-6



According to this graph reaction will be :-

- (1) Endothermic (2) Exothermic  
(3) Spontaneous at room temperature (4)  $\Delta H$  is negligible

2. For the reaction  $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$

If  $K_p = K_c (\text{RT})^x$ , when the symbols have usual meaning the value of  $x$  is (assuming ideality) :-

- (1) - 1 (2)  $-\frac{1}{2}$  (3)  $+\frac{1}{2}$  (4) + 1

3. For the equilibrium  $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$   $K_p = 63 \text{ atm}$  at 1000 K. If at equilibrium  $P_{\text{CO}} = 10 P_{\text{CO}_2}$  then total pressure at equilibrium is :-

- (1) 6.30 atm (2) 0.693 atm (3) 6.93 atm (4) 69.3 atm

4.  $\text{A}(\text{g})$  is 90 % converted in to B according to the reaction  $\text{A}(\text{g}) \rightleftharpoons 3\text{B}(\text{g})$  value of  $\left(\frac{D}{d}\right)$  at this point is :-

- (1) 1.0 (2) 2.0 (3) 2.5 (4) 2.8

5. What will be the direction of reaction if concentration of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  are  $2 \text{ mol L}^{-1}$ ,  $2 \text{ mol L}^{-1}$  and  $8 \text{ mol L}^{-1}$  respectively.  $K_c$  for reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$  is 4.

- (1) forward direction (2) backward direction  
(3) equilibrium condition (4) reaction will be completed

## ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4						
	Ans.	4	4	3	1						
BEGINNER'S BOX-2	Que.	1	2	3	4						
	Ans.	3	2	4	3						
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7			
	Ans.	4	4	2	4	1	1	4			
BEGINNER'S BOX-4	Que.	1	2	3	4	5					
	Ans.	4	1	2	1	1					
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	3	4	2	3	4	1	4	2	1
BEGINNER'S BOX-6	Que.	1	2	3	4	5					
	Ans.	1	2	3	4	2					



## EXERCISE-I (Conceptual Questions)

### FACTORS AFFECTING RATE OF REACTION

1. In an elementary reaction  $A + 2B \rightarrow 2C + D$ . If the concentration of A is increased four times and B is decreased to half of its initial concentration then the rate becomes
  - (1) Twice
  - (2) Half
  - (3) Unchanged
  - (4) One fourth of the rate
2. The role of catalyst in a chemical reaction is :-
  - (1) To help attain equilibrium in a shorter time.
  - (2) To lower the activation energy.
  - (3) To shift the equilibrium in such a way as to increase the concentration of the product
  - (4) Both 1 & 2

### EQUILIBRIUM AND CHEMICAL PROCESS

3.  $x \rightleftharpoons y$  reaction is said to be in equilibrium, when:-
  - (1) Only 10% conversion x to y takes place.
  - (2) Complete conversion of x to y takes place
  - (3) Conversion of x to y is only 50% complete
  - (4) The rate of change of x to y is just equal to the rate of change of y to x in the system
4. In the chemical reaction  $N_2 + 3H_2 \rightleftharpoons 2NH_3$  at equilibrium, state whether :-
  - (1) Equal volumes of  $N_2$  &  $H_2$  are reacting
  - (2) Equal masses of  $N_2$  &  $H_2$  are reacting
  - (3) The reaction has stopped
  - (4) The same amount of ammonia is formed as is decomposed into  $N_2$  and  $H_2$
5. Active mass of 5 g CaO :-
  - (1) 56
  - (2) 1
  - (3) 3.5
  - (4) 2
6. Ratio of active masses of 22g  $CO_2$ , 3g  $H_2$  and 7g  $N_2$  in a gaseous mixture :-
  - (1) 22 : 3 : 7
  - (2) 0.5 : 3 : 7
  - (3) 1 : 3 : 1
  - (4) 1 : 3 : 0.5

7. Which of the following example shows effect of catalyst on reversible reaction
  - (1) It gives new reaction path with low activation energy.
  - (2) It shifts equilibrium right side.
  - (3) It decrease kinetic energy of activated molecules.
  - (4) It decrease rate of backward reaction.
8. Select the correct statement from the following :
  - (1) Equilibrium constant changes with addition of catalyst
  - (2) Catalyst increases the rate of forward reaction.
  - (3) The ratio of mixture at equilibrium does not changed by catalyst
  - (4) Catalyst are active only in solution.
9. In reversible chemical reaction equilibrium will be establish when –
  - (1) Reactant completely converted into product
  - (2) Rate of forward and backward reaction is equal
  - (3) Minimum yield of product
  - (4) concentration of reactant and product is equal

### LAW OF MASS ACTION

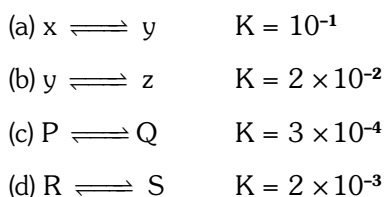
10. In a chemical equilibrium, the rate constant for the backward reaction is  $7.5 \times 10^{-4}$  and the equilibrium constant is 1.5. The rate constant for the forward reaction is:-
  - (1)  $2 \times 10^{-3}$
  - (2)  $5 \times 10^{-4}$
  - (3)  $1.12 \times 10^{-3}$
  - (4)  $9.0 \times 10^{-4}$
11. The equilibrium concentration of  $[B]_e$  for the reversible reaction  $A \rightleftharpoons B$  can be evaluated by the expression:-

(1) $K_c[A]_e^{-1}$	(2) $\frac{k_f}{k_b}[A]_e^{-1}$
(3) $k_f k_b^{-1} [A]_e$	(4) $k_f k_b [A]^{-1}$
12. In this reaction  $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$  at 298K molar concentration of  $Ag^+$ ,  $Ag(NH_3)_2^+$  and  $NH_3$  is  $10^{-1}$ ,  $10^{-1}$ , and  $10^3$ . The value of  $K_c$  at 298K for this equilibrium :-

(1) $10^{-6}$	(2) $10^6$
(3) $2 \times 10^{-3}$	(4) $2 \times 10^6$



13. Equilibrium constant of some reactions are given as under :

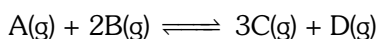


Initial concentration of the reactants for each reaction was taken to be equal :

Review the above reaction and indicate the reactions in which the reactants and products respectively were of highest concentration :-

- (1) d, c (2) c, a  
 (3) a, d (4) b, c

14. At 1000 K, the value of  $K_p$  for the reaction :



is 0.05 atm. The value of  $K_c$  in terms of R would be :-

- (1) 20000 R (2) 0.02 R  
 (3)  $5 \times 10^{-5} R$  (4)  $5 \times 10^{-5} \times R^{-1}$

15. For the reaction  $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$  the partial pressure of CO and  $CO_2$  are 2.0 and 4.0 atm respectively at equilibrium. The  $K_p$  for the reaction is  
 (1) 0.5 (2) 4.0 (3) 8.0 (4) 1

16. For which reaction is  $K_p = K_c$  :-

- (1)  $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$   
 (2)  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   
 (3)  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$   
 (4)  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

17. For the reaction



Which one is correct representation :-

- (1)  $K_p = p_{H_2O}^2$  (2)  $K_c = [H_2O]^2$   
 (3)  $K_p = K_c(RT)^2$  (4) All

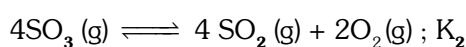
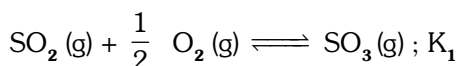
18.  $\log \frac{K_p}{K_c} + \log RT = 0$  is true relationship for the following reaction:-

- (1)  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$   
 (2)  $2SO_2 + O_2 \rightleftharpoons 2SO_3$   
 (3)  $N_2 + 3H_2 \rightleftharpoons 2NH_3$   
 (4) (2) and (3) both

19. For which reaction at 298 K, the value of  $\frac{K_p}{K_c}$  is maximum and minimum respectively:-

- (a)  $N_2O_4 \rightleftharpoons 2NO_2$   
 (b)  $2SO_2 + O_2 \rightleftharpoons 2SO_3$   
 (c)  $X + Y \rightleftharpoons 4Z$   
 (d)  $A + 3B \rightleftharpoons 7C$   
 (1) d, c (2) d, b (3) c, b (4) d, a

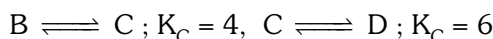
20. Consider the two gaseous equilibrium involving  $SO_2$  and the corresponding equilibrium constants at 299 K



The value of the equilibrium constant are related by :-

- (1)  $K_2 = \frac{1}{(K_1)^4}$  (2)  $K_2 = K_1^4$   
 (3)  $K_2 = \left(\frac{1}{K_1}\right)^{\frac{1}{4}}$  (4)  $K_2 = \frac{1}{K_1}$

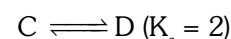
21. For the reactions :-  $A \rightleftharpoons B ; K_C = 2$ ,



$K_C$  for the reaction  $A \rightleftharpoons D$  :-

- (1) 12 (2) 4/3  
 (3) 24 (4) 48

22. If  $A \rightleftharpoons B (K_c = 3)$ ,  $B \rightleftharpoons C (K_c = 5)$ ,



The value of equilibrium constant for the above reaction are given, the value of equilibrium constant

for  $D \rightleftharpoons A$  will be:-

- (1) 15 (2) 0.3 (3) 30 (4) 0.03

23. Which Oxide of Nitrogen is most stable :-

- (1)  $2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$   
 $K = 6.7 \times 10^{16} \text{ mol L}^{-1}$   
 (2)  $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$   
 $K = 2.2 \times 10^{30}$   
 (3)  $2N_2O_{5(g)} \rightleftharpoons 2N_{2(g)} + 5O_{2(g)}$   
 $K = 1.2 \times 10^{34} \text{ mol}^5 \text{ L}^{-5}$   
 (4)  $2N_2O_{(g)} \rightleftharpoons 2N_{2(g)} + O_{2(g)}$   
 $K = 3.5 \times 10^{33} \text{ mol L}^{-1}$









35. The equilibrium constant of the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  is 64. If the volume of the container is reduced to one fourth of its original volume, the value of the equilibrium constant will be  
 (1) 16 (2) 32  
 (3) 64 (4) 128

36. If some He gas is introduced into the equilibrium  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$  at constant pressure and temperature then equilibrium constant of reaction :  
 (1) Increase  
 (2) Decrease  
 (3) Unchange  
 (4) Nothing can be said

37. **List X** **List Y**  
 (A) Active mass (I)  $\Delta n = 0$   
 (B) Dynamic nature (II) Molar concentration  
 (C)  $\text{A} + \text{heat} \rightleftharpoons \text{B}$  (III) Vant hoff's equation  
 (D)  $\log(K_{p_2}/K_{p_1})$  (IV) adaptation if temperature increases

$$= \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

- (E)  $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 3\text{C}(\text{g})$  (v) Chemical equilibrium  
 Correct match list X and Y  
 (1) A - (V), B - (II), C - (III), D - (I), E - (IV)  
 (2) A - (V), B - (IV), C - (III), D - (II), E - (I)  
 (3) A - (II), B - (V), C - (IV), D - (III), E - (I)  
 (4) None of these

#### DEGREE OF DISSOCIATION AND APPLICATION OF LAW OF MASS ACTION

38. For the reaction :  $\text{P} \rightleftharpoons \text{Q} + \text{R}$ . Initially 2 mol of P was taken. Up to equilibrium 0.5 mol of P was dissociated. What would be the degree of dissociation :-  
 (1) 0.5 (2) 1 (3) 0.25 (4) 4.2
39. The dissociation of  $\text{CO}_2$  can be expressed as  $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$ . If the 2 mol of  $\text{CO}_2$  is taken initially and 40% of the  $\text{CO}_2$  is dissociated completely. What is the total number of moles at equilibrium:-  
 (1) 2.4 (2) 2.0 (3) 1.2 (4) 5

40. In  $\text{A}_3(\text{g}) \rightleftharpoons 3\text{A}(\text{g})$  reaction, the initial concentration of  $\text{A}_3$  is "a" mol  $\text{L}^{-1}$ . If x is degree of dissociation of  $\text{A}_3$ . The total number of moles at equilibrium will be:-

- (1)  $a - \frac{ax}{3}$  (2)  $\frac{a}{3} - x$   
 (3)  $\left( \frac{a - ax}{2} \right)$  (4)  $a + 2ax$

41. In the reaction  $2\text{P}(\text{g}) + \text{Q}(\text{g}) \rightleftharpoons 3\text{R}(\text{g}) + \text{S}(\text{g})$ . If 2 mol each of P and Q taken initially in a 1 L flask. At equilibrium which is true:-  
 (1)  $[\text{P}] < [\text{Q}]$  (2)  $[\text{P}] = [\text{Q}]$   
 (3)  $[\text{Q}] = [\text{R}]$  (4) None of these

42. In a 13 L vessel initially following reaction occur  $\text{C}(\text{s}) + \text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g})$  by 12 g C, 64 g  $\text{S}_2$ , 76 g  $\text{CS}_2$  at  $1027^\circ\text{C}$  temperature then total pressure is.  
 (1) 200R (2) 158R (3) 100R (4) 79R

43. The reaction  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$  is studied in a one litre Vessel at  $250^\circ\text{C}$ . The initial concentration of A was 3n and of B was n. After equilibrium was attained then equilibrium concentration of C was found to be equal to equilibrium concentration of B. What is the concentration of D at equilibrium :-

- (1)  $\frac{n}{2}$  (2)  $\left( 3n - \frac{n}{2} \right)$   
 (3)  $\left( n + \frac{n}{2} \right)$  (4) n

44.  $\text{X}_2 + \text{Y}_2 \rightleftharpoons 2\text{XY}$  reaction was studied at a certain temperature. In the beginning 1 mole of  $\text{X}_2$  was taken in a one litre flask and 2 moles of  $\text{Y}_2$  was taken in another 2 litre flask. What is the equilibrium concentration of  $\text{X}_2$  and  $\text{Y}_2$  ? (Given equilibrium concentration of  $[\text{XY}] = 0.6 \text{ mol L}^{-1}$ ).

- (1)  $\left( \frac{1}{3} - 0.3 \right), \left( \frac{2}{3} - 0.3 \right)$   
 (2)  $\left( \frac{1}{3} - 0.6 \right), \left( \frac{2}{3} - 0.6 \right)$   
 (3)  $(1 - 0.3), (2 - 0.3)$   
 (4)  $(1 - 0.6), (2 - 0.6)$



45. If the initial pressure of  $N_2$  and  $H_2$  mixture in a closed apparatus is 100 atm. At equilibrium 20% of the mixture reacts then total pressure at the same temperature would be -  
 (1) 100 (2) 90 (3) 85 (4) 80
46. In a 20 litre vessel initially 1 - 1 mole  $CO$ ,  $H_2O$ ,  $CO_2$  is present, then for the equilibrium of  $CO + H_2O \rightleftharpoons CO_2 + H_2$  following is true:-  
 (1)  $H_2$ , more than 1 mole  
 (2)  $CO$ ,  $H_2O$ ,  $H_2$  less than 1 mole  
 (3)  $CO_2$  &  $H_2O$  both more than 1 mole  
 (4) All of these
47. 4 mol of  $PCl_5$  are heated at constant temperature in closed container. If degree of dissociation for  $PCl_5$  is 0.5 then calculate total number of moles at equilibrium  
 (1) 4.5 (2) 6 (3) 3 (4) 4
48.  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$   
 In above reaction, at equilibrium condition mole fraction of  $PCl_5$  is 0.4 and mole fraction of  $Cl_2$  is 0.3. Then find out mole fraction of  $PCl_3$   
 (1) 0.3 (2) 0.7 (3) 0.4 (4) 0.6
49. If 8 mol of  $PCl_5$  heated in a closed vessel of 10 L capacity and 25% of its dissociates into  $PCl_3$  and  $Cl_2$  at the equilibrium then value of  $K_p$  will be equal to:-  
 (1)  $P/30$  (2)  $P/15$  (3)  $2/3P$  (4)  $3/2P$
50. In the reaction  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$  the partial pressure of  $PCl_3$ ,  $Cl_2$  and  $PCl_5$  are 0.3, 0.2 and 0.6 atm respectively at equilibrium. If partial pressure of  $PCl_3$  and  $Cl_2$  was increased twice, what will be the partial pressure of  $PCl_5$  is in atm at new equilibrium condition :-  
 (1) 0.3 (2) 1.2 (3) 2.4 (4) 0.15
51. 'a' mol of  $PCl_5$ , undergoes, thermal dissociation as:  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ , the mole fraction of  $PCl_3$  at equilibrium is 0.25 and the total pressure is 2.0 atm. The partial pressure of  $Cl_2$  at equilibrium is :-  
 (1) 2.5 (2) 1.0 (3) 0.5 (4) None
52. In a 0.25 L tube dissociation of 4 mol of  $NO$  is take place. If its degree of dissociation is 10%. The value of  $K_p$  for reaction  $2 NO \rightleftharpoons N_2 + O_2$  is :-  
 (1)  $\frac{1}{(18)^2}$  (2)  $\frac{1}{(8)^2}$  (3)  $\frac{1}{16}$  (4)  $\frac{1}{32}$
53. In a chemical equilibrium  $A + B \rightleftharpoons C + D$  when one mole each of the two reactants are mixed, 0.4 mol each of the products are formed. The equilibrium constant is :-  
 (1) 1 (2) 0.36 (3) 2.25 (4)  $\frac{4}{9}$
54.  $K_c$  for the esterification reaction :  
 $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$  is 4. If 4 mol each of acid and alcohol are taken initially, what is the equilibrium concentration of the acid :-  
 (1)  $\frac{2}{3}$  (2)  $\frac{4}{3}$  (3)  $\frac{3}{4}$  (4)  $\frac{3}{2}$
55. Evaluate  $K_p$  for the reaction :  $H_2 + I_2 \rightleftharpoons 2HI$ . If 2 moles each of  $H_2$  and  $I_2$  are taken initially. At equilibrium moles of  $HI$  are 2.  
 (1) 2.5 (2) 4 (3) 0.25 (4) 1.0
56. 4 moles of A are mixed with 4 moles of B, when 2 mol of C are formed at equilibrium, according to the reaction,  $A + B \rightleftharpoons C + D$ . The equilibrium constant is :-  
 (1) 4 (2) 1 (3)  $\sqrt{2}$  (4)  $\sqrt{4}$
57. Two moles of ammonia is introduced in a evacuated 500 mL vessel at high temperature. The decomposition reaction is :  
 $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$   
 At the equilibrium  $NH_3$  becomes 1 mole then the  $K$  would be :-  
 (1) 0.42 (2) 6.75 (3) 1.7 (4) 1.5
58. 4.5 mol each of hydrogen and iodine heated in a sealed 10 litre vessel. At equilibrium, 3 mol of  $HI$  were found. The equilibrium constant for  $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$  is:-  
 (1) 1 (2) 10  
 (3) 5 (4) 0.33
59. 1.50 mol each of hydrogen and iodine were placed in a sealed 10 L container maintained at 717 K. At equilibrium 1.25 mol each of hydrogen and iodine were left behind. The equilibrium constant,  $K_c$  for the reaction  
 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  at 717 K is  
 (1) 0.4 (2) 0.16  
 (3) 25 (4) 50



60. AB dissociates as  $2AB(g) \rightleftharpoons 2A(g) + B_2(g)$   
When the initial pressure of AB is 500 mm, the total pressure becomes 625 mm when the equilibrium is attained. Calculate  $K_p$  for the reaction assuming volume remains constant.  
(1) 500 (2) 125 (3) 750 (4) 375

### LE-CHATLIER'S PRINCIPLE

61. Cis -2- pentene  $\rightleftharpoons$  Trans -2- pentene for the above equilibrium the value of standard free energy change at 400 K is  $-3.67 \text{ kJ mol}^{-1}$ . If excess of trans -2- pentene is added to the system then :-  
(1) Additional trans -2- pentene will form  
(2) Excess of cis -2- pentene will form  
(3) Equilibrium will proceed in the forward  
(4) Equilibrium will remain unaffected
62. When  $\text{NaNO}_3$  is heated in a closed vessel,  $\text{O}_2$  is liberated and  $\text{NaNO}_2$  is left behind. At equilibrium -  
(1) Addition of  $\text{NaNO}_3$  favours forward reaction  
(2) Addition of  $\text{NaNO}_2$  favours reverse reaction  
(3) Increasing pressure favours reverse reaction.  
(4) Decreasing temperature favours forward reaction.
63. The equilibrium  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$  shifts forward if :-  
(1) A catalyst is used.  
(2) An adsorbent is used to remove  $\text{SO}_3$  as soon as it is formed.  
(3) Small amounts of reactants are used.  
(4) None
64. In manufacture of NO, the reaction of  $\text{N}_2$  and  $\text{O}_2$  to form NO is favourable if :-  
(1) Pressure is increased  
(2) Pressure is decreased  
(3) Temperature is increased  
(4) Temperature is decreased
65. In which of the following equilibrium reactions, the equilibrium would shift to right side, if total pressure is decreased :-  
(1)  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  (2)  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$   
(3)  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  (4)  $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$
66. The oxidation of  $\text{SO}_2$  by  $\text{O}_2$  to  $\text{SO}_3$  is exothermic reaction. The yield of  $\text{SO}_2$  will be minimum if :-  
(1) Temperature is increased and pressure is kept constant  
(2) Temperature is reduced and pressure is increased  
(3) Both temperature and pressure are increased  
(4) Both temperature and pressure are decreased
67. For the manufacture of ammonia by the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 + 21.9 \text{ k Cal}$ , the favourable conditions are :-  
(1) Low temperature, low pressure & catalyst  
(2) Low temperature, high pressure & catalyst  
(3) High temperature, low pressure & catalyst  
(4) High temperature, high pressure & catalyst
68. In the reaction  $2\text{A}_{(g)} + \text{B}_{(g)} \rightleftharpoons \text{C}_{(g)} + 362 \text{ kCal}$ . Which combination of pressure and temperature gives the highest yield of C at equilibrium:-  
(1) 1000 atm and  $500^\circ\text{C}$   
(2) 500 atm and  $500^\circ\text{C}$   
(3) 1000 atm and  $50^\circ\text{C}$   
(4) 500 atm and  $100^\circ\text{C}$
69. Does Le chatelier's principle predict a change of equilibrium concentration for the following reaction if the gas mixture is compressed  
 $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$   
(1) Yes, backward reaction is favoured  
(2) Yes, forward reaction is favoured  
(3) No change  
(4) No information
70.  $a\text{A} \rightleftharpoons b\text{B} + c\text{C}$ ,  $\Delta H = -x \text{ kCal}$ .  
If high pressure and low temperature are the favourable condition for the formation of the product in above reaction, hence:-  
(1)  $a > b + c$  (2)  $a < b + c$   
(3)  $a = b + c$  (4) None of them
71. The reaction in which yield of production cannot be increased by the application of high pressure is :-  
(1)  $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$   
(2)  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$   
(3)  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$   
(4)  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
72. In a vessel containing  $\text{SO}_3$ ,  $\text{SO}_2$  and  $\text{O}_2$  at equilibrium, some helium gas is introduced so that the total pressure increases while temperature and volume remain constant. According to Le-Chatelier principle, the dissociation of  $\text{SO}_3$ ,  
(1) Increases  
(2) Decreases  
(3) Remains unaltered  
(4) None of these



### PHYSICAL EQUILIBRIUM

73. For the equilibrium reaction,  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ ,  
What happens, if pressure is applied:-  
(1) More water evaporates  
(2) The boiling point of water is increased  
(3) No effect on boiling point  
(4) None of the above
74. On cooling of following system at equilibrium  
 $\text{CO}_{2(\text{s})} \rightleftharpoons \text{CO}_{2(\text{g})}$  :-  
(1) There is no effect on the equilibrium state  
(2) More gas is formed  
(3) More gas is solidifies  
(4) None of above

### CALCULATION OF DEGREE OF DISSOCIATION BY V.D. METHOD

75. Vapour density of  $\text{PCl}_5$  is 104.25 at  $t^\circ\text{C}$ . Then degree of dissociation of  $\text{PCl}_5$  is. (Mw = 208.5)  
(1) 20% (2) 0% (3) 30% (4) 15%
76. When heating  $\text{PCl}_5$  then it decompose  $\text{PCl}_3$  and  $\text{Cl}_2$  in form of gas, The vapour density of gas mixture is 70.2 and 57.9 at  $200^\circ\text{C}$  and  $250^\circ\text{C}$ . The degree of dissociation of  $\text{PCl}_5$  at  $200^\circ\text{C}$  and  $250^\circ\text{C}$  is  
(1) 48.50% & 80% (2) 60% & 70%  
(3) 70% & 80% (4) 80% & 90%

77. Vapour density of  $\text{PCl}_5$  is 104.16 but when heated to  $230^\circ\text{C}$  its vapour density is reduced to 62. The degree of dissociation of  $\text{PCl}_5$  at this temperature will be :  
(1) 6.8% (2) 68% (3) 46% (4) 64%

78. The equation  $\alpha = \frac{D-d}{(n-1)d}$  is correctly matched for

Where D = Theoretical vapour density  
d = Observed vapour density

(1)  $\text{A} \rightleftharpoons \frac{n\text{B}}{2} + \frac{n\text{C}}{3}$

(2)  $\text{A} \rightleftharpoons \frac{n\text{B}}{3} + \left(\frac{2n}{3}\right)\text{C}$

(3)  $\text{A} \rightleftharpoons \left(\frac{n}{2}\right)\text{B} + \left(\frac{n}{4}\right)\text{C}$

(4)  $\text{A} \rightleftharpoons \left(\frac{n}{2}\right)\text{B} + \text{C}$

### EXERCISE-I (Conceptual Questions)

### ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	4	4	4	2	4	1	3	2	3	3	1	2	4	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	4	2	2	1	4	4	1	3	1	3	2	1	1	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	1	3	3	3	3	3	3	1	4	1	1	1	1	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	2	2	1	2	3	3	1	4	2	2	2	2	1	2	2
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	2	3	2	3	3	2	2	3	1	1	2	3	2	3	2
Que.	76	77	78												
Ans.	1	2	2												

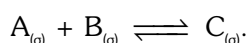


## Directions for Assertion &amp; Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.  
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.  
 (C) If Assertion is True but the Reason is False.  
 (D) If both Assertion & Reason are false.

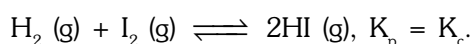
1. **Assertion :-** There is no effect on equilibrium constant if inert gas is added to the reaction



**Reason :-** Equilibrium constant changes only with temperature.

- (1) A (2) B (3) C (4) D

2. **Assertion :-** For the reaction



**Reason :-**  $K_p$  of all gaseous reactions is equal to  $K_c$ .

- (1) A (2) B (3) C (4) D

3. **Assertion :-**  $K_p = K_c$  for all reactions.

**Reason :-** At constant temperature, the pressure of the gas is proportional to the concentration.

- (1) A (2) B (3) C (4) D

4. **Assertion :-** The value of  $K$  increases when concentration of the reactants are increased.

**Reason :-** With increases of concentration of reactants the equilibrium shifts in forward direction.

- (1) A (2) B (3) C (4) D

5. **Assertion :-** The effect of temperature on equilibrium constant is given by vant Hoff's equation.

**Reason :-** vant Hoff's equation is

$$\log \frac{K_1}{K_2} = \frac{\Delta H}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

- (1) A (2) B (3) C (4) D

6. **Assertion :-** Effect of temperature on  $K_c$  or  $K_p$  depends on enthalpy change.

**Reason :-** Increase in temperature shifts the equilibrium in exothermic direction and decrease in temperature shifts the equilibrium position in endothermic direction.

- (1) A (2) B (3) C (4) D

7. **Assertion :-** On opening a sealed soda bottle dissolved carbon dioxide gas escapes.

**Reason :-** Gas escapes to reach the new equilibrium condition of lower pressure.

- (1) A (2) B (3) C (4) D

8. **Assertion :-** Solubility of a gas in liquids increases with increase in pressure of the gas in equilibrium with solution.

**Reason :-** The dissolution of a gas in liquids is an exothermic process.

- (1) A (2) B (3) C (4) D

9. **Assertion :-** Solubility of a gas in water decreases with increase in temperature.

**Reason :-** Dissolution of a gas in water is an exothermic process.

- (1) A (2) B (3) C (4) D

10. **Assertion :-** Catalyst affects the final state of the equilibrium.

**Reason :-** It enables the system to attain a new equilibrium state by complexing with the reagents.

- (1) A (2) B (3) C (4) D

11. **Assertion :-** For the reaction  $A \rightleftharpoons B + C + x \text{ kCal}$  at equilibrium state  $[A] = [B] = [C] = 3 \times 10^{-4} \text{ M}$  and equilibrium constant is  $3 \times 10^{-4}$ .

**Reason :-** Given reaction is exothermic.

- (1) A (2) B (3) C (4) D

12. **Assertion :-** For a reaction  $A_{(g)} + B_{(g)} \rightleftharpoons AB_{(g)}$  if inert gas is added in a container at constant volume. The equilibrium shifts to left side.

**Reason :-** Because partial pressure of A, B and AB decreases.

- (1) A (2) B (3) C (4) D

## EXERCISE-II (Assertion &amp; Reason)

## ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12
Ans.	1	3	4	4	3	3	1	2	1	4	2	4

